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Abstract

PROBLEM TO BE SOLVED: To relax stress generated in a thin film, and improve adhesion to the thin film, and further raise the film developing rate on a substrate by the Atomic Layer Epitaxy(ALE) method.

SOLUTION: In forming Al2O3 film by ALE method using TMA and H2O on a glass substrate, CH3OH evaporated before forming film or during formation of film is introduced and surface treatment for increasing surface hydroxyl group concentration of the ground surface is carried out by exposing the ground surface in gas atmosphere of CH3OH.

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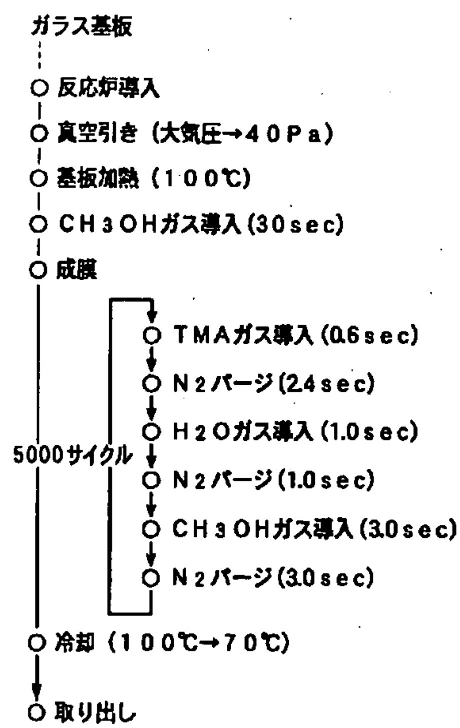
最終頁に続く

(54)【発明の名称】　薄膜の形成方法

(57)【要約】

【課題】　基板上にＡＬＥ法により薄膜を形成する薄膜の形成方法において、薄膜に発生する応力を緩和するとともに、薄膜の下地に対する密着性を向上させ、更に、成膜レートを向上させる。

【解決手段】　ガラス基板上にＴＭＡとH_2Oを用いたＡＬＥ法によりAl_2O_3膜を形成するにあたって、成膜前及び成膜中に気化したCH_3OHを導入し、下地面を、CH_3OH分子の気体雰囲気中に暴露することにより、下地面の表面水酸基濃度を高める表面処理を行う。



【特許請求の範囲】

【請求項1】　基板上に原子層成長法により薄膜を形成する方法であって、前記薄膜の成膜中及び成膜前の少なくとも一方の時期に、下地面に対して表面水酸基濃度を高める表面処理を行うことを特徴とする薄膜の形成方法。

【請求項2】　前記表面処理は、前記薄膜の原料とは異なる材料を用いて行うことを特徴とする請求項1に記載の薄膜の形成方法。

【請求項3】　前記表面処理は、前記下地面を、水酸基を持つ分子の気体雰囲気中に暴露することによりなされることを特徴とする請求項1または2に記載の薄膜の形成方法。

【請求項4】　前記水酸基を持つ分子の気体は、当該分子をプラズマ化させた状態としたものであることを特徴とする請求項3に記載の薄膜の形成方法。

【請求項5】　前記表面処理は、前記薄膜の成膜前に、前記下地面に対して、水酸基を持つ分子の液体を噴霧することによりなされることを特徴とする請求項1または2に記載の薄膜の形成方法。

【請求項6】　前記水酸基を持つ分子が、H_2O、H_2O_2、アルコール類またはこれらの2種以上を組み合わせたものであることを特徴とする請求項3ないし5のいずれか1つに記載の薄膜の形成方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、基板上に原子層成長法（Atomic Layer Epitaxy）により薄膜を形成する薄膜の形成方法に関する。

【0002】

【従来の技術】原子層成長法（Atomic Layer Epitaxy、以下、ALE法という）は、2種以上の原料（元素または化合物）を交互に供給して、基板表面の吸着反応、原料と目的生成物との蒸気圧の差を利用することにより、1原子層または1分子層ずつ結晶成長させる方法である。

【0003】

【発明が解決しようとする課題】ALE法においては、原料ガス分子の吸着機構は、Langmuir型であらわせるような自己制御型の吸着機構が支配的な場合に限られる。Langmuir型吸着機構では、原料の分圧Piのもとで、原料の表面被覆率をθi、吸着速度定数をKa、脱離速度定数をKdとすると、吸着速度はKaPi（1−θi）、脱離速度はKdθiで表される。ここで、吸着速度と脱離速度は等しいので、K＝（Ka／Kd）とすると、原料の表面被覆率θiは、次の数式1にて示される。

【0004】

【数1】$\theta i = KaPi / (Kd + KaPi) = KPi / (1 + KPi)$

ここで、KPiが1より十分大きい、即ち、気相に存在する原子または分子の量が吸着量に対し過飽和状態になっていれば、単原子層または単分子層形成が可能となる。

【0005】しかしながら、KPiを1より十分大きい状態としても、ほとんどの場合、下地面において、吸着の立体障害や吸着サイトが不均一であり、単原子層または単分子層形成は実現されない。例えば、$AlCl_3$とH_2Oとの反応によって500℃程度でALE法により層を成長させると、0.045nm／サイクルの成膜レートとなり、これは1分子層分に満たない。

【0006】このことは、反応確率が低いことやガス流れ等により、局所的にKPiが1より十分大きくないことが原因である可能性も考えられるが、次に述べるように表面吸着率の低下が大きいことが主原因であると考えられる。まず、ALE成長過程では、下地面に吸着している元素または化合物が、次に吸着する元素や化合物と反応する。

【0007】この時、系によっては、次に吸着する元素や化合物が、既に吸着している複数の元素や化合物と反応する。つまり、次に吸着する1個の元素や化合物が、複数の吸着サイトに既に吸着している元素や化合物と反応し結合するため、生成した目的生成物の結合力（分子間力やファンデルワールス力）が、近接する吸着サイトに吸着した元素または化合物にも働くので微視的な歪みが生ずる。

【0008】そして、下地面に吸着している結合は、重力や静電気力等にて吸着する物理吸着を除くと水素結合などの強い結合であるため、上記の歪みは非常に大きいものとなる。これが原因でALE法にて成膜を続けると、結果として、出来上がった薄膜において、膜が収縮しようとするいわば引っ張り応力が発生すると考えられる。

【0009】ここで、このような複数の吸着サイト間に結合力が及ぶ場合、たとえ全ての吸着サイトに均一に吸着がなされた場合であっても、上記理由により薄膜内に微視的な歪みが多少生じる。特に、下地面への吸着が不均一である場合、やはり同様に反応するが、この場合、微小空孔（元素等が吸着すべき吸着サイトであって吸着がなされていない部分により生じる空孔）が存在する。

【0010】この微小空孔は、通常、反応後の目的生成物の原子間距離よりも大きいため、近接元素または化合物に働く結合力は、より大きくなる。従って、吸着が不均一である場合には、上記の微視的な歪みも大きくなり、問題となってくる。また、下地面への吸着が不均一であると、薄膜の密着性が低下するのは明らかである。さらに、吸着が不均一となることで、成膜領域において部分的に成膜レートが遅い部分が生じ、結果的に全体の成膜レートが遅くなる。

【0011】以上のように、本発明者等の検討によれ

ば、ALE法はその成長機構から、優れた表面被覆率を持つ薄膜を得ることが可能ではあるが、その元素または化合物の下地面への吸着の不完全性から、本質的に薄膜に引っ張り応力が発生し、薄膜のクラックや剥離といった問題が生じ、また、薄膜の密着性の低下や成膜レートが遅いといった問題も生じる。

【0012】本発明は上記問題に鑑み、基板上にALE法により薄膜を形成する薄膜の形成方法において、薄膜に発生する応力を緩和するとともに、薄膜の下地に対する密着性を向上させ、更に、成膜レートを向上させることを目的とする。

【0013】

【課題を解決するための手段】本発明は、ALE法により成膜を行う前または成膜中に、下地面に対して、ガスの吸着サイトの表面密度を高める処理を行えばよいのではないかとの考えに基づいてなされたものである。

【0014】吸着サイトを決定付けるものは、下地面上の水酸基である。これは、水酸基は水素結合による大きな結合力を発生するため、下地に近づいてくる元素や化合物を引きつけ、吸着しやすくできるためである。即ち、下地面を水酸基化させる水酸基化終端処理を行うことで、吸着サイトの表面密度を向上でき、薄膜の原料ガスの吸着を促進させることができる。

【0015】例えば、下地面がTiO_2の場合、この下地面をH_2Oの気体に暴露させることにより、下地面に表面水酸基が生ずる過程は、図5のように考えられる。配位不飽和な表面Ti_4^+イオンに吸着したH_2Oは、隣接するO_2^-と水素結合をし、さらに、吸着H_2OのOH結合の切断により2つの表面水酸基が生成される。他の酸化物についても、ほぼ同様な機構でH_2Oの化学吸着により表面水酸基が生成すると考えられる。

【0016】請求項1～請求項6記載の発明は、このような考えに基づいて実験検討を行った結果、見出されたものであり、基板上に原子層成長法により薄膜を形成する方法であって、薄膜の成膜中及び成膜前の少なくとも一方の時期に、下地面に対して表面水酸基濃度を高める表面処理を行うことを特徴としている。

【0017】それによれば、下地面における吸着サイトの表面密度を向上でき、薄膜原料ガスの吸着を促進させることができるため、下地面に対する元素や化合物の吸着がより均一化する。従って、薄膜に発生する応力を緩和するとともに、薄膜の下地に対する密着性を向上させ、更に、成膜レートを向上させることができる。

【0018】また、請求項2の発明では、上記の表面処理は、薄膜の原料とは異なる材料を用いて行うことを特徴としている。この表面処理は、薄膜形成のための反応には直接関与しないように、薄膜原料の導入時期とはタイミングをずらして行うが、本発明のように、薄膜原料とは異なる材料を用いれば、当該表面処理を、より好適に薄膜形成反応に関与しないようにすることができる。

【0019】ここで、上記の表面処理は、下地面を、水酸基を持つ分子の気体雰囲気中に暴露すること（請求項3の発明）で行うことができる。この場合、水酸基を持つ分子の気体を、当該分子をプラズマ化させた状態としたもの（請求項4の発明）とすれば、上記表面処理をより効率的に行うことができる。また、上記表面処理は、薄膜の成膜前に、下地面に対して、水酸基を持つ分子の液体を噴霧すること（請求項5の発明）で行うこともできる。

【0020】また、これらの表面処理方法に用いる水酸基を持つ分子としては、H_2O、H_2O_2、アルコール類またはこれらの2種以上を組み合わせたものを、採用することができる。

【0021】なお、上記各手段の括弧内の符号は、後述する実施形態に記載の具体的手段との対応関係を示す一例である。

【0022】

【発明の実施の形態】基板上に原子層成長法（ALE法）により薄膜を形成する方法は、反応炉内に基板を設置し、反応炉内へ、薄膜の原料ガスを導入することによりなされる。ここにおいて、下地面に対して表面水酸基濃度を高める表面処理（以下、単に表面処理という）の実行は、薄膜の成膜中及び成膜前の両方の時期にて行っても、成膜中のみに行っても、成膜前のみに行っても良い。

【0023】この表面処理に用いる材料としては、水酸基を持つ分子よりなる化合物を用いることができ、具体的には、H_2O、H_2O_2、アルコール類またはこれらの2種以上を組み合わせたものを採用することができる。そして、これら表面処理用材料を用いた表面処理の方法としては、次のような方法を採用することができる。

【0024】まず、予め、水酸基を持つ分子よりなる化合物を気化して、下地面をこの気体（水酸基を持つ分子の気体）雰囲気に暴露する方法が挙げられる。例えば、メタノールや水等の水酸基を持つ化合物の入った原料ボトルを加熱などして気化させ、N_2やArなどのキャリアガスで、基板が入っている反応炉に導入すれば良い。それにより、基板における薄膜の下地面が水酸基を持つ分子の気体雰囲気中に暴露され、下地面に対して上記表面処理が施される。

【0025】ここで、水酸基を持つ分子の気体を、当該分子をプラズマ化させた状態としたものとすれば、上記表面処理をより効率的に行うことができる。即ち、反応炉内において、対向して離間配置された一対の電極を設け、これら電極の間に基板を設置して高周波電圧を印加した状態で、水酸基を持つ分子の気体を導入する。すると、当該分子がプラズマ化される（例えばCH_3OHでは、OH^-やOHラジカルが生じる）ため、より活性な反応が基板上で可能となり、効率的な表面処理が可能となる。

【0026】また、水酸基を持つ分子よりなる化合物の液体を、下地面に対して噴霧するようにしても良い。例えば、インジェクタなどを用いて、基板が配置された反応炉内へ噴霧することが可能である。ただし、この場合は、上記した下地面を水酸基を持つ分子の気体雰囲気に暴露する方法に比べて、物理吸着する化合物が非常に多く、これがALE法による層成長を阻害する。

【0027】そのため、基板を若干加熱したりN_2やArガスなどの雰囲気にしたりして、この物理吸着分を除去することが望ましい。さらには、真空にした反応炉内に、水酸基を持つ化合物の液体を適量噴霧すれば、急激な断熱膨張により気化するため、より効率的に噴霧による表面処理が可能となる。

【0028】次に、本実施形態について具体例を示しながら、更に説明する。ガラス基板上にTMA（テトラメチルアルミニウム、$AlCl_3$）とH_2Oにより、薄膜としてAl_2O_3膜をALE成長させながら、メタノール（CH_3OH）の気体暴露による表面処理を行った場合と行わない場合（比較例）とを示す。

【0029】まず、ガラス基板上にTMAとH_2Oを用いたALE法によりAl_2O_3膜を形成する薄膜の形成方法において、Al_2O_3膜の成膜前及び成膜中に、CH_3OHによる表面処理を行った場合（本実施形態の具体例）を示す。そのフローを図1に示す。

【0030】40mm×40mm、厚さ1．1mmのガラス製基板を、反応炉に入れた。その反応炉を40Pa程度の真空にし、N_2ガスを400sccm程度流しながら基板を加熱し基板温度を100℃に安定させた。CH_3OHを原料ボトル内で30℃にて気化し、N_2ガス400sccmで反応炉に30秒導入した。このCH_3OHの導入により、成膜前の表面処理を行った。

【0031】この後、TMA、H_2O、CH_3OHの順にキャリアガスであるN_2ガス400sccmで反応炉に導入した。TMAおよびH_2Oは、原料ボトル内にて室温で気化し、キャリアガスであるN_2ガス400sccmで反応炉に導入した。

【0032】反応炉へのガスは、まず気化TMAを0．6秒導入した後、パージとしてN_2ガスを2．4秒導入した。その後、同様に気化H_2Oを1．0秒、N_2パージを1．0秒のガス導入時間にて成膜した。その後、成膜中の表面処理を行うために、気化CH_3OHをN_2ガス400sccmで反応炉に3秒導入し、気相中のCH_3OHを排気するためN_2パージを3sccm行った。

【0033】このTMA導入→パージ→H_2O導入→パージ→CH_3OH導入→パージのサイクルを5000回繰り返し成膜を行った。この間、反応炉の圧力は150～320Paであり、基板温度は反応炉内のヒータによって100℃に保持した。成膜が終了した後は、N_2ガスを400sccm導入しながら、放置冷却を行い、基板温度が70℃になった時点で反応炉を大気圧にし、基板を取り出した。

【0034】この手法により、膜厚約480nmのAl_2O_3膜が得られた。この時の成膜レートは0．096nm／サイクルであった。また成膜前後のガラス基板の反り量から測定したAl_2O_3膜の応力は引っ張り応力で、220MPaであった。

【0035】次に、比較例として、ガラス基板上にTMAとH_2OによりAl_2O_3膜をALE成長させ、表面処理を行わなかった場合を示す。そのフローを図2に示す。上記と同様のサイズのガラス製基板を、反応炉に入れ、上記具体例と同様に、反応炉を40Pa程度の真空にし、N_2ガスを400sccm程度流しながら基板を加熱し基板温度を100℃に安定させた。

【0036】その後、TMA、H_2Oの順にキャリアガスであるN_2ガス400sccmで反応炉に導入した。反応炉へのガスは、まず、気化TMAを0．6秒導入した後、基板表面に吸着した分子以外の気相に存在する過剰のTMAを取り除くためのパージとしてN_2ガスを2．4秒導入した。その後、同様に気化H_2Oを1．0sec、N_2パージを4．0秒のガス導入時間にて成膜した。

【0037】このTMA導入→パージ→H_2O導入→パージのサイクルを5000回繰り返し成膜を行った。この間、反応炉の圧力は150～300Paであり、基板温度は反応炉内のヒータによって100℃に保持した。成膜が終了した後は、N_2ガスを400sccm導入しながら、放置冷却を行い、基板温度が70℃になった時点で反応炉を大気圧にし、基板を取り出した。

【0038】この手法により、膜厚約400nmのAl_2O_3膜が得られた。この時の成膜レートは0．08nm／サイクルであった。また成膜前後のガラス基板の反り量から測定したAl_2O_3膜の応力は、引っ張り応力で、430MPaであった。

【0039】図3は、上記本実施形態の具体例と比較例との結果に基づき、本発明の応力緩和の効果を具体的に示す図である。表面処理を行った方は応力が緩和されているのが分かる。また、図4は、上記本実施形態の具体例と比較例との結果に基づき、本発明の成膜レート向上の効果を具体的に示す図である。表面処理を行った場合は行わなかった場合に比べて、成膜レートは約1．2倍に速くなり、成膜レートも向上している。また、成膜レートが向上したことから、吸着が均一化し、薄膜の密着性も向上できていると言える。

【0040】このように、ALE法において、薄膜の成膜中及び成膜前の少なくとも一方の時期に、下地面に対して表面水酸基濃度を高める表面処理を行うことにより、下地面における吸着サイトの表面密度を向上でき、薄膜原料ガスの吸着を促進させることができるため、下地面に対する元素や化合物の吸着がより均一化する。従って、薄膜に発生する応力を緩和するとともに、薄膜の

下地に対する密着性を向上させ、更に、成膜レートを向上させることができる。

【0041】ここで、上記の表面処理は、薄膜の原料（上記例ではTMAやH_2O）とは異なる材料（上記例ではCH_3OH）用いて行うことにより、表面処理が、薄膜形成のための反応には直接関与しないようにすることを、好適に実現できる。なお、表面処理を薄膜原料と同じ材料で行っても良い。例えば、上記具体例の場合、表面処理をH_2Oで行っても良い。この場合、TMA導入→パージ→薄膜原料としてのH_2O導入→パージ→表面処理用材料としてのH_2O導入→パージのサイクルを行うようにすればよい。

【0042】また、表面処理用材料としては、水酸基を持つ分子以外にも、例えば、エーテル系化合物、ケトン系化合物、カルボン酸系化合物等の、エーテル結合、カルボキシル基、カルボニル基を持つ分子等から適宜選択しても良い。

【0043】なお、本発明は、例えば、基板上に、一対の電極間に有機発光層を挟んでなる構造体を配置してなる有機EL素子において、この構造体を被覆して保護する保護膜を形成する場合等に適用することができる。

【図面の簡単な説明】

【図1】本発明の実施形態に係る薄膜の形成方法を示す流れ図である。

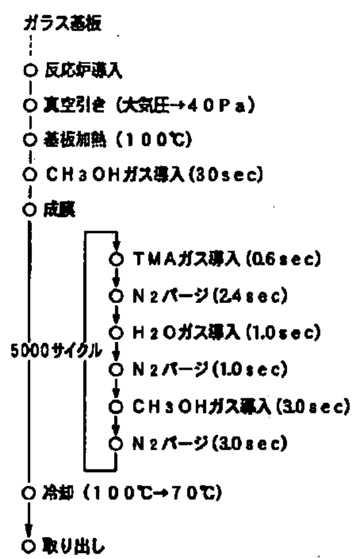
【図2】比較例としての薄膜の形成方法を示す流れ図である。

【図3】本発明の薄膜の応力緩和の効果を具体的に示す図である。

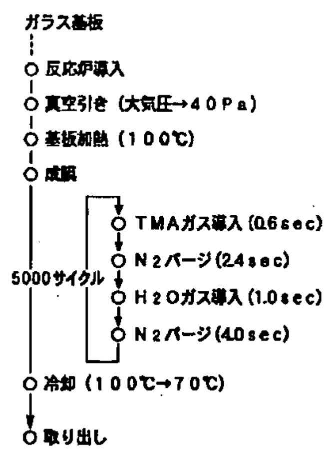
【図4】本発明の成膜レート向上の効果を具体的に示す図である。

【図5】下地面がTiO_2の場合のH_2O暴露による表面水酸基が生ずる過程の推定メカニズムを示す図である。

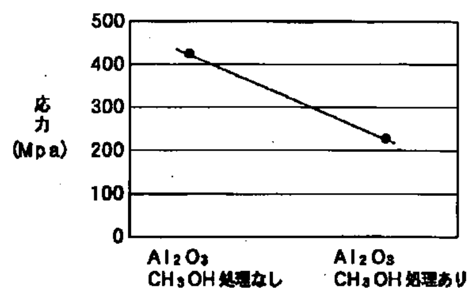
【図1】



【図2】



【図3】



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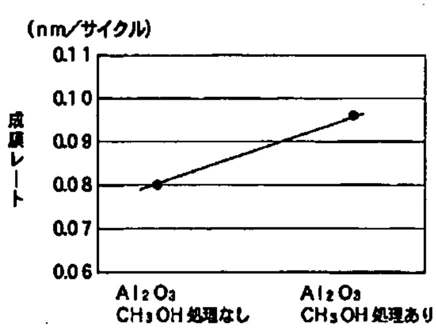
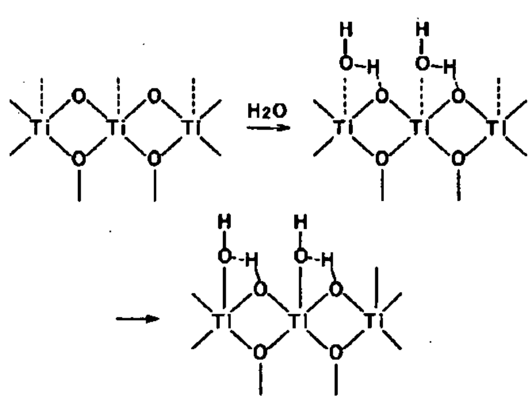


【図5】



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* NOTICES *

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1. This document has been translated by computer.So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3.In the drawings, any words are not translated.

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[Translation done.]

Summary.

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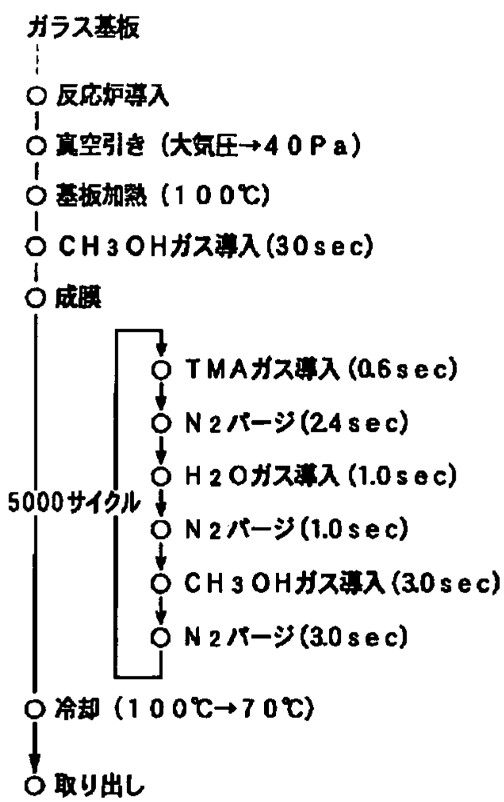
(57) [Abstract]
[Technical problem] In the formation method of the thin film which forms a thin film by the ALE method on a substrate, while easing the stress generated in a thin film, the adhesion to the ground of a thin film is raised and a membrane formation rate is raised further.
[Means for Solution] Surface treatment which raises the surface-water-of-aggregate acid-radical concentration of a ground side is performed by introducing CH3OH evaporated before membrane formation and during membrane formation, and exposing a ground side into the gas atmosphere of a CH3OH molecule in forming 2Oaluminum3 film by the ALE method which used TMA and H2O on the glass substrate.

[Translation done.]



[Translation done.]

* NOTICES *

CLAIMS

[Claim(s)]

[Claim 1] The formation method of the thin film characterized by being the method of forming a thin film by the atomic-layer grown method on a substrate, and performing surface treatment which raises surface-water-of-aggregate acid-radical concentration to a ground side at one [at least] time under membrane formation of the aforementioned thin film, and before membrane formation.

[Claim 2] For the raw material of the aforementioned thin film, the aforementioned surface treatment is the formation method of the thin film according to claim 1 characterized by carrying out using a different material.

[Claim 3] The aforementioned surface treatment is the formation method of the thin film according to claim 1 or 2 characterized by being made by exposing the aforementioned ground side into the gas atmosphere of a molecule with a hydroxyl group.

[Claim 4] The gas of a molecule with the aforementioned hydroxyl group is the formation method of the thin film according to claim 3 characterized by considering as the state where the molecule concerned was made to plasma-ize.

[Claim 5] The aforementioned surface treatment is the formation method of the thin film according to claim 1 or 2 characterized by being made by spraying the

liquid of the molecule which has a hydroxyl group to the aforementioned ground side before membrane formation of the aforementioned thin film.

[Claim 6] The claim 3 to which a molecule with the aforementioned hydroxyl group is characterized by combining H_2O, H_2O_2, alcohols, or these two sorts or more, or the formation method of the thin film any one publication of five.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the formation method of the thin film which forms a thin film by the atomic-layer grown method (Atomic Layer Epitaxy) on a substrate.

[0002]

[Description of the Prior Art] An atomic-layer grown method (it is called the ALE method Atomic Layer Epitaxy and the following) is one atomic layer or a method which carries out a crystal growth at a time one molecular layer by supplying two or more sorts of raw materials (an element or compound) by turns, and using the difference of the adsorption reaction on the front face of a substrate, and the vapor pressure of a raw material and the purpose product.

[0003]

[Problem(s) to be Solved by the Invention] In the ALE method, the adsorption mechanism of a material gas molecule is restricted, when the autogenous-control type adsorption mechanism which can be expressed with a Langmuir type is dominant. By the Langmuir type adsorption mechanism, in the surface coverage of a raw material, when thetai and a rate-of-adsorption constant are set to Ka and a desorption rate constant is set to Kd under the partial pressure Pi of a raw material, a rate of adsorption is expressed with KaPi (1-thetai), and a desorption rate is expressed with Kdthetai. Here, since a rate of adsorption and a desorption rate are equal, when K= (Ka/Kd), surface coverage thetai of a raw material is shown by the following formula 1.

[0004]

[Equation 1] thetai=KaPi/(Kd+KaPi) =KPi/(1+KPi)

Here, if KPi is larger than 1 enough, namely, the amount of the atom which exists in a gaseous phase, or a molecule is in the supersaturation state to the amount of adsorption, a monoatomic layer or monomolecular-layer formation will be attained.

[0005] However, in KPi, in almost all cases, the steric hindrance and the adsorption site of adsorption are uneven, and a monoatomic layer or monomolecular-layer formation is not realized [in / a ground side / as a sufficiently larger state than 1]. For example, by the reaction of AlCl3 and H2O, if a layer is grown up by the ALE method at about 500 degrees C, it will become the membrane formation rate of 0.045nm/a cycle, and a part for one molecular layer will not be filled with this.

[0006] Although possibility of being because KPi not being locally larger than 1 enough is also considered by things, a gas flow, etc. with low response probability, this is considered that it is the cause of main that decline in surface surface coverage is large so that it may state below. First, in an ALE growth process, the element which is sticking to a ground side, or a compound reacts with the element and compound which stick to a degree.

[0007] At this time, the element which sticks to a degree, and a compound react with two or more elements and compounds to which it has already stuck depending on a system. That is, since the bonding strength (intermolecular force and Van der Waals force) of the generated purpose product works also to the element or compound which stuck to the approaching adsorption site in order that one element and compound which stick to a degree may react to two or more adsorption sites with the element and compound to which it has already stuck and may combine with them, a microscopic distortion arises.

[0008] And since combination which is sticking to a ground side is a strong combination of hydrogen bond etc. when physical adsorption to which it sticks in gravity, an electrostatic force, etc. is removed, the above-mentioned distortion will become very large. If this continues membrane formation by the ALE method owing to, as a result, a film contracts in the done thin film, and if like is supposed and it says, it will be thought that a tensile stress occurs.

[0009] Here, when bonding strength reaches among such two or more adsorption sites, even if it is the case where adsorption is uniformly made by all adsorption sites even if, a microscopic distortion arises somewhat in a thin film for the reason for the above. Although it reacts similarly too especially when adsorption to a ground side is uneven, minute hole (hole produced by the portion in which it is the adsorption site to which an element etc. should stick, and adsorption is not made) exists in this case.

[0010] The bonding strength which commits this minute hole to a contiguity element or a compound since it is usually larger than the interatomic distance of the purpose product after a reaction becomes larger. Therefore, when adsorption is uneven, the above-mentioned microscopic distortion also becomes large and poses a problem. Moreover, it is distinct that the adhesion of a thin film falls that adsorption to a ground side is uneven. Furthermore, in a membrane formation field, a portion with a late membrane formation rate arises partially that adsorption is uneven in a bird clapper, and the whole membrane formation rate becomes late as a result.

[0011] As mentioned above, although the ALE method can obtain a thin film with the outstanding surface coverage from the growth mechanism according to this invention person's etc. examination, a tensile stress essentially occurs in a thin film, and the crack of a thin film and the problem of ablation arise from the imperfection of adsorption to the ground side of the element or a compound, and the problem that a fall and membrane formation rate of the adhesion of a thin film are late is also produced.

[0012] this invention raises the adhesion to the ground of a thin film while easing the stress generated in a thin film in view of the above-mentioned problem in the formation method of the thin film which forms a thin film by the ALE method on a substrate, and it aims at raising a membrane formation rate further.

[0013]

[Means for Solving the Problem] this invention is made based on the idea whether processing which raises the surface density of the adsorption site of gas to a ground side during membrane formation should be performed, before forming membranes by the ALE method.

[0014] It is the hydroxyl group on a ground side which determines an adsorption site. Since a hydroxyl group generates the big bonding strength by hydrogen bond, this is because it can be made easy to draw the element and compound approaching a ground and to adsorb. That is, by performing hydroxyl-group-ized termination processing in which a ground side is made to hydroxyl-group-ize, the surface density of an adsorption site can be improved and adsorption of the material gas of a thin film can be promoted.

[0015] For example, when a ground side is TiO2, the process which a surface-water-of-aggregate acid radical produces in a ground side is considered like drawing 5 by making this ground side expose to the gas of H2O. coordination -- H2O which stuck to unsaturated surface Ti4+ ion carries out adjoining O2- and hydrogen bond, and two surface-water-of-aggregate acid radicals are further generated by cutting of OH combination of adsorption H2O It is thought that a surface-water-of-aggregate acid radical generates by the chemical absorption of

$H2O$ by the almost same mechanism about other oxides.

[0016] As a result of performing experiment examination based on such an idea, invention according to claim 1 to 6 is a method which is found out and forms a thin film by the atomic-layer grown method on a substrate, and is characterized by performing surface treatment which raises surface-water-of-aggregate acid-radical concentration to a ground side at one [at least] stage under membrane formation of a thin film, and before membrane formation.

[0017] Since according to it the surface density of the adsorption site in a ground side can be improved and adsorption of thin film material gas can be promoted, the adsorption of an element and a compound to a ground side equalizes more. Therefore, while easing the stress generated in a thin film, the adhesion to the ground of a thin film can be raised and a membrane formation rate can be raised further.

[0018] Moreover, in invention of a claim 2, the above-mentioned surface treatment is characterized by carrying out using a different material from the raw material of a thin film. This surface treatment can be prevented from participating the surface treatment concerned in a thin film formation reaction more suitably, if material which is different from the introductory stage of a thin film raw material with a thin film raw material like this invention although carried out by shifting timing is used so that it may not participate in the reaction for thin film formation directly.

[0019] The here above-mentioned surface treatment can be performed by exposing a ground side into the gas atmosphere of a molecule with a hydroxyl group (invention of a claim 3). In this case, the thing (invention of a claim 4) which made the gas of a molecule with a hydroxyl group the state where the molecule concerned was made to plasma-ize, then the above-mentioned surface treatment can be performed more efficiently. Moreover, the above-mentioned surface treatment can also be performed by spraying the liquid of the molecule which has a hydroxyl group to a ground side before membrane formation of a thin film (invention of a claim 5).

[0020] Moreover, as a molecule with the hydroxyl group used for these surface treatment methods, what combined H2O, H2O2, alcohols, or these two sorts or more is employable.

[0021] In addition, the sign in the parenthesis of each above-mentioned means is an example which shows a correspondence relation with the concrete means of a publication to the operation gestalt mentioned later.

[0022]

[Embodiments of the Invention] The method of forming a thin film by the atomic-layer grown method (the ALE method) on a substrate installs a substrate in a reactor, and is made by introducing the material gas of a thin film into a reactor. In here, even if it performs execution of the surface treatment (only henceforth surface treatment) which raises surface-water-of-aggregate acid-radical concentration to a ground side with the stage of both under membrane formation of a thin film, and before membrane formation and goes only during membrane formation, you may go only before membrane formation.

[0023] The compound which consists of a molecule with a hydroxyl group as a material used for this surface treatment can be used, and, specifically, what combined H2O, H2O2, alcohols, or these two sorts or more can be adopted. And as the method of the surface treatment using the charge of these surface treatment material, the following methods are employable.

[0024] First, the compound which consists of a molecule with a hydroxyl group beforehand is evaporated, and the method of exposing a ground side to this gas (gas of molecule with hydroxyl group) atmosphere is mentioned. For example, what is necessary is for heating etc. to make it evaporate by carrying out the raw material bottle containing the compound with hydroxyl groups, such as a methanol and water, and just to introduce into the reactor in which the substrate is contained by carrier gas, such as N2 and Ar. It is exposed by that cause into the gas atmosphere of the molecule in which the ground side of the thin film in a substrate has a hydroxyl group, and the above-mentioned surface treatment is performed to a ground side.

[0025] Here, the thing which made the gas of a molecule with a hydroxyl group the state where the molecule concerned was made to plasma-ize, then the above-mentioned surface treatment can be performed more efficiently. namely, the inside of a reactor -- setting -- countering -- alienation -- the electrode of the arranged couple is prepared, and where it installed the substrate and high-frequency voltage is impressed among these electrodes, the gas of a molecule with a hydroxyl group is introduced Then, since the molecule concerned is plasma-ized (for example, OH- and OH radical arise in CH3OH), a activity reaction becomes possible on a substrate and the efficient surface treatment of it becomes possible.

[0026] Moreover, you may make it spray the liquid of the compound which consists of a molecule with a hydroxyl group to a ground side. For example, it is possible to spray into the reactor by which the substrate has been arranged using an injector etc. However, there are very many compounds which physisorb the ground side described above in this case compared with the method of exposing to the gas atmosphere of a molecule with a hydroxyl group, and this checks the layer growth by the ALE method.

[0027] Therefore, it is desirable to heat a substrate a little, or to make it atmosphere, such as N2 and Ar gas, and to remove a part for this physical adsorption. Furthermore, if optimum dose spraying of the liquid of the compound which has a hydroxyl group in the reactor made into the vacuum is carried out, in order to evaporate by rapid adiabatic expansion, the surface treatment by spraying becomes more efficiently possible.

[0028] Next, while an example is shown about this operation gestalt, it explains further. The case (example of comparison) where it does not carry out with the case where surface treatment by gas exposure of a methanol (CH3OH) is performed is shown by TMA (tetramethyl aluminum, AlCl3) and H2O on a glass substrate, carrying out ALE growth of the 2Oaluminum3 film as a thin film.

[0029] First, in the formation method of the thin film which forms 2Oaluminum3 film on a glass substrate by the ALE method which used TMA and H2O, the case

(example of this operation gestalt) where surface treatment by CH3OH is performed before membrane formation of 2Oaluminum3 film and during membrane formation is shown. The flow is shown in drawing 1 .

[0030] 40mmx40mm and the glass substrate with a thickness of 1.1mm were put into the reactor. The reactor was made into the about 40Pa vacuum, the substrate was heated for about 400 sccms of N2 gas with the sink, and substrate temperature was stabilized at 100 degrees C. CH3OH was evaporated at 30 degrees C within the raw material bottle, and it introduced into the reactor for 30 seconds by N2 gas 400sccm. This introduction of CH3OH performed surface treatment before membrane formation.

[0031] Then, it introduced into the reactor by N2 gas 400sccm which is carrier gas in order of TMA, H2O, and CH3OH. TMA and H2O were evaporated at the room temperature within the raw material bottle, and were introduced into the reactor by N2 gas 400sccm which is carrier gas.

[0032] The gas to a reactor introduced N2 gas for 2.4 seconds as a purge, after introducing Evaporation TMA for 0.6 seconds first. Then, the N2 purge was similarly formed for evaporation H2O in the gas installation time for 1.0 seconds for 1.0 seconds. Then, in order to perform surface treatment under membrane formation, evaporation CH3OH was introduced into the reactor for 3 seconds by N2 gas 400sccm, and in order to exhaust CH3OH in a gaseous phase, the N2 purge was performed 3 sccms.

[0033] This TMA introduction -> purge ->H2O introduction -> purge ->CH3OH introduction -> repeat membrane formation was performed for the cycle of a purge 5000 times. In the meantime, the pressure of a reactor is 150-320Pa, and substrate temperature was held at 100 degrees C at the heater in a reactor. After membrane formation was completed, when neglect cooling was performed and substrate temperature became 70 degrees C, carrying out 400sccm introduction of the N2 gas, the reactor was made into atmospheric pressure, and the substrate was taken out.

[0034] By this technique, 2Oaluminum3 film of about 480nm of thickness was

obtained. The membrane formation rate at this time was 0.096nm/a cycle. Moreover, the stress of 2Oaluminum3 film measured from the amount of curvatures of the glass substrate before and behind membrane formation was a tensile stress, and was 220MPa.

[0035] Next, as an example of comparison, ALE growth of the 2Oaluminum3 film is carried out by TMA and H2O on a glass substrate, and the case where surface treatment is not performed is shown. The flow is shown in drawing 2 . The same glass substrate of size as the above is put into a reactor, like the above-mentioned example, the reactor was made into the about 40Pa vacuum, the substrate was heated for about 400 sccms of N2 gas with the sink, and substrate temperature was stabilized at 100 degrees C.

[0036] Then, it introduced into the reactor by TMA and N2 gas 400sccm which is carrier gas in order of H2O. First, the gas to a reactor introduced N2 gas for 2.4 seconds as a purge for removing superfluous TMA which exists in gaseous phases other than the molecule which stuck to the substrate front face, after introducing Evaporation TMA for 0.6 seconds. Then, 1.0sec(s) and the N2 purge were similarly formed for evaporation H2O in the gas installation time for 4.0 seconds.

[0037] This TMA introduction -> purge ->H2O introduction -> repeat membrane formation was performed for the cycle of a purge 5000 times. In the meantime, the pressure of a reactor is 150-300Pa, and substrate temperature was held at 100 degrees C at the heater in a reactor. After membrane formation was completed, when neglect cooling was performed and substrate temperature became 70 degrees C, carrying out 400sccm introduction of the N2 gas, the reactor was made into atmospheric pressure, and the substrate was taken out.

[0038] By this technique, 2Oaluminum3 film of about 400nm of thickness was obtained. The membrane formation rate at this time was 0.08nm/a cycle. Moreover, the stress of 2Oaluminum3 film measured from the amount of curvatures of the glass substrate before and behind membrane formation was a tensile stress, and was 430MPa.

[0039] Drawing 3 is drawing showing the effect of the stress relaxation of this invention concretely based on the result of the example of this above-mentioned operation gestalt, and the example of comparison. The direction which performed surface treatment is understood that stress is eased. Moreover, drawing 4 is drawing showing concretely the effect of the improvement in a membrane formation rate of this invention based on the result of the example of this above-mentioned operation gestalt, and the example of comparison. When surface treatment is performed, compared with the case where it does not carry out, a membrane formation rate increases quick about 1.2 times, and its membrane formation rate is also improving. Moreover, since the membrane formation rate improved, adsorption equalizes and it can be said that the adhesion of a thin film can also be improving.

[0040] Thus, in the ALE method, since the surface density of the adsorption site in a ground side can be improved and adsorption of thin film material gas can be promoted by performing surface treatment which raises surface-water-of-aggregate acid-radical concentration to a ground side at one [at least] stage under membrane formation of a thin film, and before membrane formation, the adsorption of an element and a compound to a ground side equalizes more. Therefore, while easing the stress generated in a thin film, the adhesion to the ground of a thin film can be raised and a membrane formation rate can be raised further.

[0041] Here, the above-mentioned surface treatment can realize suitably making it not participate in the reaction for thin film formation of surface treatment directly by [from the raw material (the above-mentioned example TMA and H2O) of a thin film / different] carrying out by using material (the above-mentioned example CH3 OH). In addition, you may perform surface treatment with the same material as a thin film raw material. For example, in the case of the above-mentioned example, you may perform surface treatment by H2O. In this case, what is necessary is just made to perform the cycle of an H2O introduction -> purge as a charge of H2O introduction -> purge -> surface treatment material as a TMA

introduction -> purge -> thin film raw material.

[0042] Moreover, as a charge of surface treatment material, you may choose from the molecule with ether linkage, a carboxyl group, and a carbonyl group of for example, an ether system compound, a ketone system compound, a carboxylic-acid system compound, etc. suitably besides a molecule with a hydroxyl group.

[0043] In addition, this invention can be applied when forming the protective coat which covers and protects this structure in the organic EL element which comes to arrange the structure which comes to insert an organic luminous layer into inter-electrode [of a couple] for example, on a substrate.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the flow chart showing the formation method of the thin film concerning the operation gestalt of this invention.

[Drawing 2] It is the flow chart showing the formation method of the thin film as an example of comparison.

[Drawing 3] It is drawing showing concretely the effect of the stress relaxation of the thin film of this invention.

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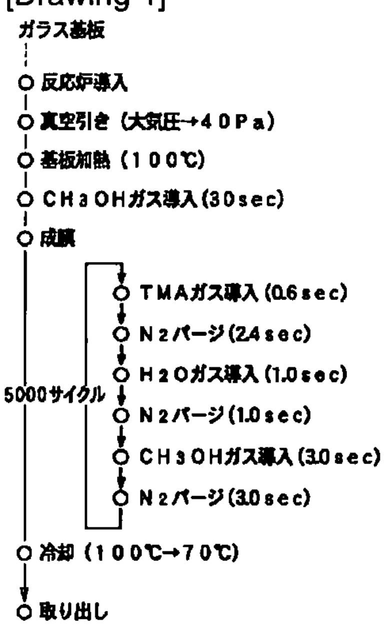
[Drawing 4] It is drawing showing concretely the effect of the improvement in a membrane formation rate of this invention.

[Drawing 5] It is drawing showing the presumed mechanism of the process which the surface-water-of-aggregate acid radical by H2O exposure in case a ground side is TiO2 produces.

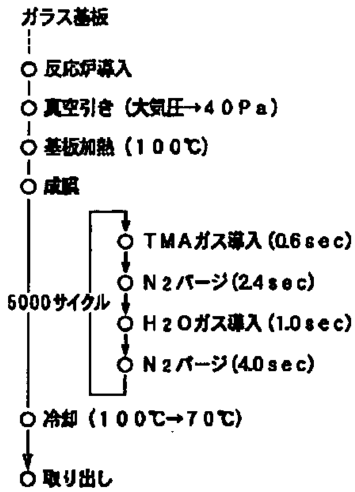
[Translation done.]

DRAWINGS

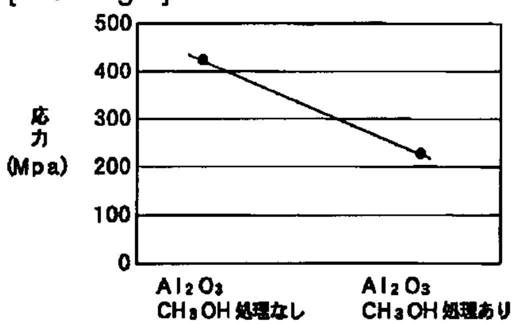
[Drawing 1]



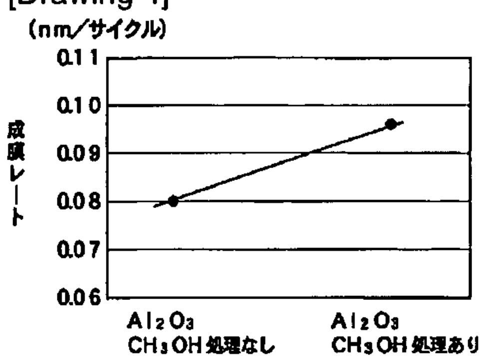
[Drawing 2]



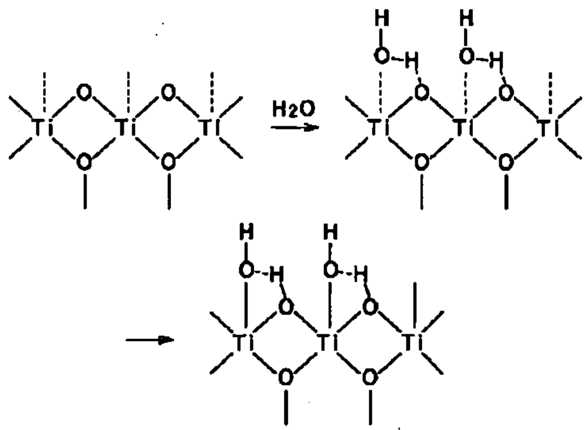
[Drawing 3]



[Drawing 4]



[Drawing 5]



[Translation done.]